

OFFICE OF NAVAL RESEARCH  
END-OF-THE-YEAR REPORT  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT : N00014-95-1-1182

PR Number (Reed) 96PR01651

**Self-Assembly Based Approaches to Microelectronic Fabrication and Devices:  
Surface Passivation, Soft Lithography, Electrically Functional Systems,  
and Hierarchical Self-Assembly**

PIs:

David Allara, Pennsylvania State University  
George Maracas, Motorola  
Mark Reed, Yale University (coordinator)  
James Tour, University of South Carolina  
George Whitesides, Harvard University

contact address:

Department of Electrical Engineering, Yale University  
P. O. Box 208284  
New Haven, CT 06520

Date Submitted: June 28, 1996

November 17, 1997

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OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR01651

Contract/Grant Number: N00014-95-1-1182

Contract/Grant Title: "Self-Assembly Based Approaches to Microelectronic Fabrication and Devices: Surface Passivation, Soft Lithography, Electrically Functional Systems, and Hierarchical Self-Assembly"

Principal Investigators:

David Allara, Pennsylvania State University

George Maracas, Motorola

Mark Reed, Yale University (coordinator)

James Tour, University of South Carolina

George Whitesides, Harvard University

Mailing Addresses:

David L. Allara

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E-mail Address: [dla3@psu.edu](mailto:dla3@psu.edu)

http address: none

George Maracas

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Phone Number: (602) 413-6384

Fax Number: (602) 413-7281

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http address: none

Mark A. Reed

Dept. of Electrical Engineering, Yale University, P. O. Box 208284, New Haven, CT 06520

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Fax Number: (203) 432-7769

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http address: <http://surf.eng.yale.edu/~reed>

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Fax Number: 803-777-9521

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http address: <http://www.cosm.sc.edu/chem/tour.html>

George M. Whitesides

Department of Chemistry, Harvard University, 12 Oxford Street , Cambridge MA 02139  
Phone Number: (617) 495 9430  
Fax Number: (617) 495 9857  
E-mail Address: [gwhitesides@gmwgroup.harvard.edu](mailto:gwhitesides@gmwgroup.harvard.edu)  
http address: none

## Part I

Sections are listed in full under each of the investigators, separately

### Allara

Principal Investigator: D.L Allara

Mailing Address: 185 MRI Bldg. Penn State U., University Park. PA

Phone Number: (814) 865-2254

Fax Number: (814) 863-0618

E-mail Address: dla3@psu.edu

http address:

- a. Number of papers submitted to refereed journals, but not published: \_\_\_\_
- b. + Number of papers published in refereed journals (for each, provide a complete citation):  
    1  
    "Are Single Molecular Wires Conducting?," L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones II, D.L. Allara, J.M. Tour and P.S. Weiss, *Science*, 271, 1705-1707(1996)
- c. + Number of books or chapters submitted, but not yet published: \_\_\_\_
- d. + Number of books or chapters published (for each, provide a complete citation): \_\_\_\_
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): \_\_\_\_
- f. Number of patents filed: \_\_\_\_
- g. + Number of patents granted (for each, provide a complete citation): \_\_\_\_
- h. + Number of invited presentations (for each, provide a complete citation): 2  
    1.) American Physical Society annual meeting, Kansas City, March 1997. "Probing Electronic Properties of Single Molecules."  
    2.) **Materials Research Society, annual meeting, Boston, "Self-Assembly Strategies for Fabrication of Molecule-Based Devices,"** D. Allara, T. Dunbar, P. Weiss, M. Cygan, L. Bumm, Dept. of Chemistry, Pennsylvania State University, University Park, PA; J. Tour, T. Burgin, Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, SC; M. Reed, R. Lombardi, Yale U.
- i. + Number of submitted presentations (for each, provide a complete citation): \_\_\_\_
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 1  
    Elected Fellow of the American Association for the Advancement of Science (AAAS)  
    (This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 2  
    Graduate Students: 2  
    Post-Doctoral Associates: \_\_\_\_  
    including the number of,  
        Female Graduate Students: 1  
        Female Post-Doctoral Associates: \_\_\_\_  
    the number of  
        Minority\* Graduate Students: \_\_\_\_  
        Minority\* Post-Doctoral Associates: \_\_\_\_  
    and, the number of  
        Asian Graduate Students: \_\_\_\_

Asian Post-Doctoral Associates: \_\_\_\_\_

1. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)  
No new grants)

## Maracas

Principal Investigator: George Maracas

Mailing Address: Motorola, 2100 East Elliot Road, Tempe, AZ 85284

Phone Number: (602) 413-6384 Fax Number: (602) 413-7281

E-mail Address: george-maracas\_a524aa@email.mot.com

http address: none

- a. Number of papers submitted to refereed journals, but not published: \_\_\_\_
- b. + Number of papers published in refereed journals (for each, provide a complete citation): \_\_\_\_
- c. + Number of books or chapters submitted, but not yet published: \_\_\_\_
- d. + Number of books or chapters published (for each, provide a complete citation): \_\_\_\_
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): \_\_\_\_
- f. Number of patents filed: \_\_\_\_
- g. + Number of patents granted (for each, provide a complete citation): \_\_\_\_
- i. + Number of invited presentations (for each, provide a complete citation): \_\_\_\_
- i. + Number of submitted presentations (for each, provide a complete citation): \_\_\_\_
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): \_\_\_\_  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: N/A  
Graduate Students: N/A  
Post-Doctoral Associates: \_\_\_\_  
including the number of,  
Female Graduate Students: \_\_\_\_  
Female Post-Doctoral Associates: \_\_\_\_  
the number of  
Minority\* Graduate Students: \_\_\_\_  
Minority\* Post-Doctoral Associates: \_\_\_\_  
and, the number of  
Asian Graduate Students: \_\_\_\_  
Asian Post-Doctoral Associates: \_\_\_\_
- c. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

## Reed

Principal Investigator: Mark A. Reed

Mailing Address: Dept. of Electrical Engineering, Yale University, P. O. Box 208284, New Haven, CT 06520

Phone Number: (203) 432-4306

Fax Number: (203) 432-7769

E-mail Address: reed@surf.eng.yale.edu

http address: <http://surf.eng.yale.edu/~reed>

- a. Number of papers submitted to refereed journals, but not published: 2
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 5
- c. + Number of books or chapters submitted, but not yet published: 2
- d. + Number of books or chapters published (for each, provide a complete citation): 0
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. + Number of patents granted (for each, provide a complete citation): 0
- h. + Number of invited presentations (for each, provide a complete citation): 5
- i. + Number of submitted presentations (for each, provide a complete citation): 0
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 0  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 96PR01651
  - Graduate Students: 4
  - Post-Doctoral Associates: 0
  - including the number of,
  - Female Graduate Students: 2
  - Female Post-Doctoral Associates: 0
  - Minority\* Graduate Students: 0
  - Minority\* Post-Doctoral Associates: 0.25
  - Asian Graduate Students: 2
  - Asian Post-Doctoral Associates: 0
- l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published.

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

## PART I

### a. Papers submitted to refereed journals (and not yet published):

Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. "Conductance of a Molecular Junction", *Science*, under review.

Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L., II; Tour, J. M. "Fabrication of Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures", *Appl. Phys. Lett.*, in press.

### b. Papers published in refereed journals:

Muller, C. J.; Vleeming, B. J.; Reed, M. A.; Lamba, J. J. S.; Hara, R.; Jones, L., II; Tour, J. M. "Atomic Probes: a Search for Conduction Through a Single Molecule", *Nanotechnology* **1996**, *7*, 409-411.

"There is plenty of room between two atom contacts", C.J. Muller and M.A. Reed, *Science*. **272**, 1901 (1996).

J.W. Sleight, E.S. Hornbeck, M.R. Deshpande, R.G. Wheeler, M.A. Reed, R.C. Bowen, W.R. Frensley, J.N. Randall, and R.J. Matyi, "Electron-spectroscopic study of vertical  $\text{In}_{1-x}\text{Ga}_x\text{As}$  quantum dots", *Phys. Rev.* **B53**, 15727 (1996).

M.R. Deshpande, J.W. Sleight, M.A. Reed, and R.G. Wheeler, "Zeeman splitting of single semiconductor impurities in resonant tunneling heterostructures", *Superlattices and Microstructures* **20**, 513 (1996).

M.R. Deshpande, J.W. Sleight, M.A. Reed, R.G. Wheeler, and R.J. Matyi, "Spin splitting of single 0D impurity states in semiconductor heterostructure quantum wells", *Phys. Rev. Lett.* **76**, 1328 (1996).

### c. Books or chapters submitted, but not yet published:

"Conductance Quantization in Fully Integrated Break Junctions at Room Temperature", C. Zhou, C.J. Muller, M.R. Deshpande, J. McCormack, and M.A. Reed, in *Nanowires* (eds. P.A. Serena and N. Garcia, Kluwer, the Netherlands, 1997).

"Mesoscopic Phenomena Studied with Mechanically Controllable Break Junctions at Room Temperature", C. Zhou, C.J. Muller, M.A. Reed, T.P. Burgin, J.M. Tour, in *Molecular Electronics* (eds. J. Jortner and M. Ratner, Blackwell Science, Oxford, United Kingdom, 1997).

### d. Books or chapters published: none

### e. Technical Reports Published and Papers Published in Non-Refereed Journals: none



f. Patents Filed: none

g. Patents Granted: none

h. Invited Presentations:

1. "Conductance Measurements of Single Atoms and Molecular Systems", AVS meeting, Philadelphia, October 1996.
2. "Novel compressed functionality circuits", Advanced Heterostructure Transistors, Kohala, Hawaii, December 1994.
3. "Interband tunneling device structures", Advanced Heterostructure Transistors, Kohala, Hawaii, December 1994.
4. "Conductance of molecular junctions", Meeting of the American Physical Society, Kansas City, Missouri, 17-21 March, 1997.
5. "Transport in molecular systems", Colloquia, at CEA-Saclay, Paris, France, 9 March 1997.

i. Submitted Presentations: None.

j. Honors/Awards/Prizes: none

l. Other Funding: none

## Tour

Principal Investigator: James M. Tour

Mailing Address: University of South Carolina, Department of Chemistry and Biochemistry,  
Columbia, SC 29208

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Fax Number: 803-777-9521

E-mail Address: tour@psc.sc.edu

http address: www.jmtour.com

- a. Number of papers submitted to refereed journals, but not published: 5
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 7
- c. + Number of books or chapters submitted, but not yet published: 1
- d. + Number of books or chapters published (for each, provide a complete citation): 0
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. + Number of patents granted (for each, provide a complete citation): 0
- h. + Number of invited presentations (for each, provide a complete citation): 19
- i. + Number of submitted presentations (for each, provide a complete citation): 0
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 5  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 96PR01651
  - Graduate Students: 2.8
  - Post-Doctoral Associates: 2.0
  - including the number of,
  - Female Graduate Students: 0.4
  - Female Post-Doctoral Associates: 0
  - Minority\* Graduate Students: 0.3
  - Minority\* Post-Doctoral Associates: 0.4
  - Asian Graduate Students: 0.83
  - Asian Post-Doctoral Associates: 0.75
- l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)
  - + Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published.
  - \* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

## PART I

### a. Papers submitted to refereed journals (and not yet published):

Zacarias, A. G.; Castro, M.; Seminario, J. M.; Tour, J. M. "Lowest Energy States of Pd<sub>4</sub> Using DFT: Nanotips for Single Molecule Electronics", *Chem. Phys. Lett.*, under review.

Seminario, J. M.; Tour, J. M. "Systematic Study of the Lowest Energy States of Au<sub>n</sub> (n = 1-4): Understanding Gold Contacts for Molecular Scale Electronics", *J. Int. Quant. Chem.*, under review.

Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. "Conductance of a Molecular Junction", *Science*, under review.

Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. "Insertion, Conductivity, and Structure of Conjugated Organic Oligomers in Self-Assembled Alkanethiol Monolayers on Au{111}", *J. Am. Chem. Soc.* under review.

Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L., II; Tour, J. M. "Fabrication of Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures", *Appl. Phys. Lett.*, in press.

### b. Papers published in refereed journals:

Pearson, D. L.; Jones, L., II; Schumm, J. S.; Tour, J. M. "Molecular Scale Electronics. Syntheses and Testing", *Synth. Metals* **1997**, *84*, 303-306.

Jones, L., II; Schumm, J. S.; Tour, J. M. "Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene-ethynylene)s With Thioester Termini: Molecular Scale Wires With Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support", *J. Org. Chem.* **1997**, *62*, 1388-1410.

Pearson, D. L.; Tour, J. M. "Rapid Syntheses of Oligo(2,5-thiophene-ethynylene)s with Thioester Termini: Potential Molecular Scale Wires With Alligator Clips", *J. Org. Chem.* **1997**, *62*, 1376-1387.

Schumm, J. S.; Pearson, D. L.; Jones, L., II; Hara, R.; Tour, J. M. "Potential Molecular Wires and Molecular Alligator Clips", *Nanotechnology* **1996**, *7*, 430-433.

Muller, C. J.; Vleeming, B. J.; Reed, M. A.; Lamba, J. J. S.; Hara, R.; Jones, L., II; Tour, J. M. "Atomic Probes: a Search for Conduction Through a Single Molecule", *Nanotechnology* **1996**, *7*, 409-411.

Jones, L., II; Tour, J. M. "Solid-Phase Synthesis of Potential Molecular Wires. Attachment of Molecular Alligator Clips", in *Electrical, Optical, and Magnetic Properties of Organic Solid*

*State Materials*, Dalton, L.; Jen, A. K. Y.; Wnek, G. E.; Rubner, M. F.; Lee, C. Y.-C., Chiang, L. Y., Eds., *Mater. Res. Soc. Proc.* **1996**, *413*, 401-406.

Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. "Convergent Synthetic Routes to Orthogonally Fused Conjugated Oligomers Directed Toward Molecular Scale Electronic Device Applications", *J. Org. Chem.* **1996**, *61*, 6906-6921.

c. Books or chapters submitted, but not yet published:

Pearson, D. L.; Jones, L.; Schumm, J. S.; Tour, J. M. "Synthesis of Molecular Scale Wires and Alligator Clips", NATO Advanced Research Workshop, *Applied Science Series*, Joachim, C. and Roth, S. Eds., Kluwer: Dordrecht, Netherlands, in press.

d. Books or chapters published: none

e. Technical Reports Published and Papers Published in Non-Refereed Journals: none

f. Patents Filed: none

g. Patents Granted: none

h. Invited Presentations:

1. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Gordon Research Conference on Polymer Chemistry, New Hampshire, June 15, 1996.
2. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Albemarle Corporation, June 19, 1996.
3. Conjugated Oligomers and Polymers for Molecular Scale Electronic Applications. Synthetic Metals Conference, Salt Lake City, UT, July 30, 1996.
4. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Maxdem Corporation, September 23, 1996.
5. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. California Institute of Technology, September 24, 1996.
6. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. University of California at Irvine, September 25, 1996.
7. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. University of California at Los Angeles, September 26, 1996.
8. Conjugated Oligomers and Polymers for Molecular Scale Electronic Applications. Defense Advanced Research Projects Agency Conference, Estes Park, CO, October 10, 1996.

9. Conjugated Oligomers and Polymers for Molecular Scale Electronic Applications. SERMACS Conference, Greenville, SC, November 11, 1996. Invited Lecture.
10. Conjugated Oligomers and Polymers for Molecular Scale Electronic Applications. SERMACS Conference, Greenville, SC, November 11, 1996.
11. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. University of Rochester, November 22, 1996.
12. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. George Washington University, December 6, 1996.
13. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Milliken Corporation, December 13, 1996.
14. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Tulane University, January 29, 1997.
15. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Clemson University, February 7, 1997.
16. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. University of Alabama, March 13, 1997.
17. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Colorado State University, March 24, 1997.
18. Synthesis of Conjugated Oligomers and Polymers for Electronic and Photonic Applications. Duke University, April 11, 1997.
19. Molecular Electronics. Syntheses and Testing. Naval Research Laboratories, Washington, DC, May 15, 1997.

i. Submitted Presentations: None.

j. Honors/Awards/Prizes:

1. Governor's Mathematics and Science Advisory Board for South Carolina, September 1996 to present.
2. Guy F. Lipscomb Professor of Chemistry, University of South Carolina, Columbia, SC, August 1996 to present.
3. National Science Foundation, Materials Research Centers Advisory Committee, Princeton University, February 1997.
4. Russell Research Award in Science, Mathematics and Engineering, Univ. South Carolina, May 1997.
5. National Science Foundation, Presidential Young Investigator Award, Materials Division/Polymers, 1991-96.

l. Other Funding:

Active Support:

1. Office of Naval Research, "Synthesis of Polymeric Families with Highly Delocalized Electronic States for Electronic and Photonic Applications", 10/1/95-9/30/98, \$270,000. No relation to this DARPA grant.

2. Department of Defense/ASSERT, "ARPA Augmentation Proposal", 9/1/93-8/31/96, \$150,327, via Larry Cooper for further developments of the above molecular electronics systems.
3. Federal Aviation Administration, "Synthesis and Characterization of New Flame Resistant Materials", written with M. Angel, 9/1/95- 8/31/98, \$175,300 for J. Tour. The FAA funds one student plus some equipment. No relation to this DARPA grant.
4. Department of Energy, EPSCoR, "Electrochemical Cells based on Fullerene Nanotubes", 10/15/95-10/14/97, \$152,000 for J. Tour. No relation to this DARPA grant.
5. National Science Foundation, Synthesis of Precise Unnatural Oligomers Using Well-Defined Synthetic and DNA Templates", 7/1/96-6/30/97, \$50,000. PI, F146. No relation to this DARPA grant, though the techniques could be useful for preparing molecular wires.
6. National Science Foundation/ARI, "Departmental NMR Console Upgrades", 1997, co-PI on this departmental grant. No relation to this DARPA grant.
7. National Science Foundation/EPSCoR, "Fundamental Studies at Polymer/Materials Interfaces: A Junior Faculty Development Proposal in Optical Sensing", 9/1/96-8/81/99, \$950,000, co-PI with several faculty, acting as the faculty mentor, ~\$15,000 in summer salary to J. Tour. No relation to this DARPA grant.

OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number:

Contract/Grant Number: N00014-95-1-1182

Contract/Grant Title: Self-assembly in Microelectronics Fabrication: Surface  
Passivation; Soft Lithography; Electronically Functional Systems; Hierarchical  
Self-Assembly

Principal Investigator: George M. Whitesides

Mailing Address: 12 Oxford St., Cambridge, MA 02138

Phone Number: 617-495-9430 Fax Number: 617-495-9857

E-mail Address: gwhitesides@gmwgroup.harvard.edu

http address: <http://www.chem.harvard.edu/GeorgeWhitesides.html>

- a. Number of papers submitted to refereed journals, but not published: 16
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 46
- c. + Number of books or chapters submitted, but not yet published: 0
- d. + Number of books or chapters published (for each, provide a complete citation):  
0
- e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 1
- g. + Number of patents granted (for each, provide a complete citation):
- h. + Number of invited presentations (for each, provide a complete citation):  
3
- i. + Number of submitted presentations (for each, provide a complete citation):  
0
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 2  
Madison Marshall Award (American Chemical Society)  
Member, American Philosophical Society  
Defense Advanced Research Projects Agency Award for  
Significant Technical Achievement, 1996
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 3  
Graduate Students: 2  
Post-Doctoral Associates: 1  
including the number of,  
Female Graduate Students: 1  
Female Post-Doctoral Associates: 0  
the number of  
Minority\* Graduate Students: 0  
Minority\* Post-Doctoral Associates: 0  
and, the number of  
Asian Graduate Students: 1  
Asian Post-Doctoral Associates: 1

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

**General Distribution List (abstracts only):**

(PI list: Use email distribution list sent via email)

#### **Technical Report Distribution List**

Dr. John C. Pazik (1)\*  
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Ft. Belvoir, VA 22060-6218

Director, Naval Research Laboratory (1)  
Attn: Code 2627  
4555 Overlook Ave.  
Washington, DC 20375-5326



## EOY Report - PART I

### a. Papers submitted to refereed journals, but not published

Mrksich, M., and G. M. Whitesides, submitted 1996, Using Self-Assembled Monolayers that Present Oligo (ethylene glycol) Groups to Control the Interactions of Proteins with Surfaces, ACS Volume on Chemistry and Biological Applications of Polyethylene Glycol.

Mrksich, M., L. E. Dike, J. Tien, D. E. Ingber, and G. M. Whitesides, submitted 1996, Using Microcontact Printing to Pattern the Attachment of Mammalian Cells to Self-Assembled Monolayers of Alkanethiolates on Transparent Films of Gold and Silver, Exp. Cell Research.

Terfort, A., and G. M. Whitesides, submitted 1997, Self-Assembly of an Operating Electrical Circuit Based on Shape Complementary and the Hydrophobic Effect: Adv. Mater.

Rogers, J. A., K. E. Paul, R. J. Jackman, and G. M. Whitesides, submitted 1997, Generating ~90 Nanometer Features Using Near-Field Contact-Mode Photolithography With an Elastomeric Phase Mask: J. Vac. Sci. Tech.

Zhao, X.-M., S. P. Smith, S. J. Waldman, G. M. Whitesides, and M. Prentiss, submitted 1997, Demonstration of Waveguide Couplers Fabricated Using Microtransfer Molding: Appl. Phys. Lett.

Qin, D., Y. Xia, A. J. Black, and G. M. Whitesides, submitted 1997, Photolithography With Transparent Reflective Photomasks: J. Vac. Sci. & Technol. B.

Yan, L., J. Rao, and G. M. Whitesides, submitted 1997, Using Surface Plasmon Resonance to Study the Binding of Vancomycin and Its Dimer to Self-Assembled Monolayers Presenting D-Ala-D-Ala: J. Am. Chem. Soc.

Tien, J., A. Terfort, and G. M. Whitesides, submitted 1997, Microfabrication Through Electrostatic Self-Assembly: Langmuir.

Karim, A., J. F. Douglas, E. J. Amis, J. A. Rogers, R. J. Jackman, and G. M. Whitesides, submitted 1997, Phase Separation of Ultrathin Polymer Blend Films on Chemically Patterned SAM Substrates: Phys. Rev. Lett.

Rogers, J. A., K. E. Paul, and G. M. Whitesides, submitted 1997, Quantifying Distortions in Soft Lithography: J. Vac. Sci. Tech.

Tien, J., Y. Xia, and G. M. Whitesides, submitted 1997, Microcontact Printing of SAMs: book Chapter, ed., Abraham Ulman.

Xia, Y., and G. Whitesides, submitted 1997, Soft Lithography: Angew. Chem. Int. Ed. Engl.

Xia, Y., N. Venkateswaran, D. Qin, J. Tien, and G. M. Whitesides, submitted 1997, The Use of Electroless Silver as the Substrate in Microcontact Printing of Alkanethiols, and Its Application in Microfabrication: Langmuir.

Yan, L., C. Marzolin, A. Terfort, and G. Whitesides, M, submitted 1997, Formation and Reaction of Interchain Carboxylic Anhydride Groups on Self-Assembled Monolayers on Gold: Langmuir.

Roberts, C., C. Chen, M. Mrksich, V. Martichonok, D. Ingber, and G. Whitesides, submitted 1997, Using Mixed Self-Assembled Monolayers Presenting GRGD and EG3OH Groups to Characterize Long-term Attachment of Bovine Capillary Endothelial Cells to Surfaces: J. Am. Chem. Soc.

Jackman, R., S. Brittain, and G. Whitesides, submitted 1997, Fabrication of Three-Dimensional Microstructures by Electrochemically Welding Structures formed by Microcontact Printing on Planar and Curved Substrates: J. MEMS.

**b. Papers published in refereed journals**

Xia, Y., E. Kim, M. Mrksich, and G. M. Whitesides, 1996, Microcontact Printing of Alkanethiols on Copper and Its Application in Microfabrication: Chem. Mat., v. 8, p. 601-603.

Deng, L., M. Mrksich, and G. M. Whitesides, 1996, Self-Assembled Monolayers of Alkanethiolates Presenting Tri(propylenesulfoxide) Groups Resist the Adsorption of Protein: Journal of the American Chemical Society, v. 118, p. 5136-5137.

Zhao, X.-M., Y. Xia, and G. M. Whitesides, 1996, Fabrication of Three-Dimensional Micro-Structures: Microtransfer Molding: Adv. Mater., v. 8, p. 837-840.

Zhao, X.-M., J. L. Wilbur, and G. M. Whitesides, 1996, Using Two-Stage Chemical Amplification to Determine the Density of Defects in Self-Assembled Monolayers of Alkanethiolates on Gold: Langmuir, v. 12, p. 3257-3264.

Sigal, G. B., C. Bamdad, A. Barberis, J. Strominger, and G. M. Whitesides, 1996, A Self-Assembled Monolayer for the Binding and Study of Histidine-Tagged Proteins by Surface Plasmon Resonance: Analytical Chemistry, v. 68, p. 490-497.

Hidber, P. C., W. Helbig, E. Kim, and G. M. Whitesides, 1996, Microcontact Printing of Palladium Colloids: Micron-Scale Patterning by Electroless Deposition of Copper: Langmuir, v. 12, p. 1375-1380.

Kim, E., and G. M. Whitesides, 1997, Imbibition and Flow of Wetting Liquids in Noncircular Capillaries: J. Phys. Chem., v. 101, p. 855-863.

Qin, D., Y. Xia, and G. M. Whitesides, 1996, Rapid Prototyping of Complex Structures with Feature Sizes Larger than 20  $\mu\text{m}$ : *Adv. Mater.*, v. 8, p. 917-919.

Whitesides, G. M., E. E. Simanek, and C. B. Gorman, 1996, Approaches to Synthesis Based on Non-Covalent Bonds, in C. Chatgililoglu, and V. Snieckus, eds., *NATO Advanced Study Institute on Chemical Synthesis: Gnosis to Prognosis*, Dordrecht, Kluwer Academic Publishers, p. 565/88.

Mammen, M., K. Helmersen, R. Kishore, S.-K. Choi, W. D. Phillips, and G. M. Whitesides, 1996, Optically Controlled Collisions of Biological Objects to Evaluate Potent Polyvalent Inhibitors of Virus-Cell Adhesion: *Chem. & Biol.*, v. 3, p. 757-763.

Xia, Y., X.-M. Zhao, and G. M. Whitesides, 1996, Pattern Transfer: Self-Assembled Monolayers as Ultrathin Resists: *Microelec. Eng.*, v. 32, p. 255-268.

Rogers, J. A., R. J. Jackman, G. M. Whitesides, J. L. Wagner, and A. Vengsarkar, 1997, Using Microcontact Printing to Generate Amplitude Photomasks on the Surfaces of Optical Fibers: A New Method for Producing In-Fiber Gratings: *Appl. Phys. Lett.*, v. 70, p. 2464-2466.

Zhao, X.-M., A. Stoddart, S. P. Smith, E. Kim, Y. Xia, M. Prentiss, and G. M. Whitesides, 1996, Fabrication of Single-Mode Polymeric Waveguides Using Micromolding in Capillaries: *Adv. Mater.*, v. 8, p. 420-424.

Xia, Y., E. Kim, and G. M. Whitesides, 1996, Micromolding of Polymers in Capillaries: Applications in Microfabrication: *Chem. Mat.*, v. 8, p. 1558-1567.

Kim, E., Y. Xia, and G. M. Whitesides, 1996, Micromolding in Capillaries: Applications in Materials Science: *J. Am. Chem. Soc.*, v. 118, p. 5722-5731.

Xia, Y., E. Kim, X.-M. Zhao, J. A. Rogers, M. Prentiss, and G. M. Whitesides, 1996, Complex Optical Surfaces by Replica Molding against Elastomeric Masters: *Science*, v. 273, p. 347-349.

Mrksich, M., C. S. Chen, Y. Xia, L. E. Dike, D. E. Ingber, and G. M. Whitesides, 1996, Controlling Cell Attachment on Contoured Surfaces with Self-Assembled Monolayers of Alkanethiolates on Gold: *Proc. Natl. Acad. U.S.A.*, v. 93, p. 10775-10778.

Xia, Y., E. Kim, and G. M. Whitesides, 1996, Microcontact Printing of Alkanethiols on Silver and Its Application in Microfabrication: *J. Electrochem. Soc.*, v. 143, p. 1070-1079.

Weisbecker, C. S., and G. M. Whitesides, 1996, Molecular Self-Assembly of Aliphatic Thiols on Gold Colloids: *Langmuir*, v. 12, p. 3763-3772.

Cyr, D. M., B. Venkataraman, G. W. Flynn, A. Black, and G. M. Whitesides, 1996, Functional Group Identification in Scanning Tunneling Microscopy of Molecular Adsorbates: *J. Phys. Chem.*, v. 100, p. 13747-13759.

Xia, Y., and G. M. Whitesides, 1996, Shadowed Sputtering of Gold on V-Shaped Microtrenches Etched in Silicon and Applications in Microfabrication: *Adv. Mater.*, v. 8, p. 765-768.

Hidber, P. C., P. F. Nealey, W. Helbig, and G. M. Whitesides, 1996, A New Strategy for Controlling the Size and Shape of Metallic Features Formed by Electroless Deposition of Copper: Microcontact Printing of Catalysts on Oriented Polymers, Followed by Thermal Shrinkage: *Langmuir*, v. 12, p. 5209-15.

Xia, Y., J. Tien, D. Qin, and G. M. Whitesides, 1996, Non-Photolithographic Methods for Fabrication of Elastomeric Stamps for Use in Microcontact Printing: *Langmuir*, v. 12, p. 4033-4038.

Nealey, P. F., A. J. Black, J. L. Wilbur, and G. M. Whitesides, in press 1996, Micro- and Nanofabrication Techniques Based on Self-Assembled Monolayers, in J. Jortner, and M. Ratner, eds., *Molecular Electronics*, Oxford, Blackwell Science.

Wilbur, J. L., A. Kumar, H. A. Biebuyck, E. Kim, and G. M. Whitesides, 1996, Microcontact Printing of Self-Assembled Monolayers: Applications in Microfabrication: *Nanotechnology*, v. 7, p. 452-457.

Whidden, T. K., D. K. Ferry, M. N. Kozicki, E. Kim, A. Kumar, J. L. Wilbur, and G. M. Whitesides, 1996, Pattern Transfer to Silicon by Microcontact Printing and RIE: *Nanotechnology*, v. 7, p. 447-451.

Wilbur, J. L., and G. M. Whitesides, in press 1996, Self-Assembly and Self-Assembled Monolayers in Micro- and Nanofabrication, in G. Timp, ed., *Nanotechnology*.

Kim, E., G. M. Whitesides, M. B. Freiler, M. Levy, J. L. Lin, and R. M. Osgood, 1996, Fabrication of Micrometer-Scale Structures on GaAs and GaAs/AlGaAs Quantum Well Material Using Microcontact Printing: *Nanotechnology*, v. 7, p. 266-269.

Xia, Y., D. Win, and G. M. Whitesides, 1996, Microcontact Printing with a Cylindrical Rolling Stamp: A Practical Step Toward Automatic Manufacturing of Patterns with Submicrometer-Sized Features: *Adv. Mater.*, v. 8, p. 1015-1017.

Xia, Y., J. J. McClelland, R. Gupta, D. Qin, X.-M. Zhao, L. L. Sohn, R. J. Celotta, and G. M. Whitesides, 1997, Replica Molding Using Polymeric Materials: A Practical Step Toward Nanomanufacturing: *Adv. Mater.*, v. 9, p. 147-9.

Zhao, X.-M., Y. Xia, D. Qin, and G. M. Whitesides, 1997, Fabrication of Polymeric Microstructures With High Aspect Ratios Using Shrinkable Polystyrene Films: *Adv. Mater.*, v. 9, p. 251-4.

Rogers, J. A., R. J. Jackman, and G. M. Whitesides, 1997, Microcontact Printing and Electroplating on Curved Substrates: A Means for Producing Free-Standing Three-Dimensional Microstructures with Possible Applications Ranging from Micro-Coil Springs to Coronary Stents: *Adv. Mater.*, v. 9, p. 475-7.

Xia, Y., and G. M. Whitesides, 1997, Extending Microcontact Printing as a Microlithographic Technique: *Langmuir*, v. 13, p. 2059-2067.

Jackman, R. J., J. A. Rogers, and G. M. Whitesides, 1997, Fabrication and Characterization of a Concentric, Cylindrical Microtransformer: *IEEE Trans. Magnetics*, v. 33, p. 2501-2503.

Sigal, G. B., M. Mrksich, and G. M. Whitesides, 1997, Using Surface Plasmon Resonance Spectroscopy to Measure the Association of Detergents with Self-Assembled Monolayers of Hexadecanethiolate on Gold: *Langmuir*, v. 13, p. 2749-2755.

Terfort, A., N. Bowden, and G. M. Whitesides, 1997, Three-dimensional self-assembly of millimetre- scale components: *Nature*, v. 386, p. 162-164.

Schueller, O. J. A., S. T. Brittain, and G. M. Whitesides, 1997, Fabrication of Glassy Carbon Microstructures by Pyrolysis of Microfabricated Polymeric Precursors: *Adv. Mater.*, v. 9, p. 477-480.

Rogers, J. A., K. E. Paul, R. J. Jackman, and G. M. Whitesides, in press 1997, Using an Elastomeric Phase Mask for Sub-100 nm Photolithography in the Optical Near Field: *Appl. Phys. Lett.*

Qin, D., Y. Xia, and G. M. Whitesides, 1997, Elastomeric Light Valves: *Adv. Mater.*, v. 9, p. 407-10.

Kim, E., Y. Xia, X.-M. Zhao, and G. M. Whitesides, in press 1997, Solvent-Assisted Microcontact Molding: A Convenient Method for Fabricating Three-Dimensional Structures on Surfaces of Polymers: *Adv. Mater.*

Rogers, J. A., R. J. Jackman, G. M. Whitesides, D. L. Olson, and J. V. Sweedler, 1997, Using Microcontact Printing to Fabricate Microcoils on Capillaries for High Resolution Proton Nuclear Magnetic resonance on Nanoliter Volumes: *Appl. Phys. Lett.*, v. 70, p. 2464-2466.

Schueller, O. J. A., S. T. Brittain, C. Marzolin, and G. M. Whitesides, 1997, Fabrication and Characterization of Glassy Carbon MEMS: *Chem. Mater.*, v. 9, p. 1399-1406.

Zhao, X.-M., X. Younan, and G. M. Whitesides, 1997, Soft Lithographic Methods for Nanofabrication: *J. Mat. Chem.*, v. 7, p. 1069-1074.

Chen, C. S., M. Mrksich, S. Huang, G. M. Whitesides, and D. E. Ingber, 1997, Geometric Control of Cell Life and Death: Science, v. 276, p. 1425-1428.

Sigal, G. B., M. Mrksich, and G. M. Whitesides, in press 1997, The Effect of Surface Hydrophobicity on the Adsorption of Proteins and Detergents: J. Am. Chem. Soc.

Marzolin, C., A. Terfort, J. Tien, and G. M. Whitesides, in press 1997, Patterning of a Polysiloxane Precursor to Silicate Glasses by Microcontact Printing: Thin Solid Films.

#### **h. Invited Presentations**

##### Named Lectureships

- Redman Lectures; Hamilton, Toronto, Canada (11/18-19/96)
- Purvis Lectures, McGill University, Canada (3/17-18/97)
- Robinson Lectures, Oxford University, UK (5/19-23/97)
- Condon Lecture, University of Colorado, Boulder, CO (10/11/97)

##### Invited Speaker

- Gordon Conference, New England College, Henniker, NH (6/24/96)
- Defense Science Research Council Summer Conference; La Jolla, CA (7/7/96-8/2/96)
- American Institute of Chemical Engineers 5th World Congress of Chemical Engineering; San Diego, CA (7/17/96)
- American Chemical Society Young Chemists Committee; Orlando, FL (8/26-27/96)
- American Chemical Society - Lackritz Symposium; Orlando, FL (8/28-9/96)
- Moët-Hennessy/ Louis Vuitton Lecture: Shape and Science (9/10/96)
- Cornell University, Ithaca, NY (9/25/96)
- ULTRA Electronics Review, Estes Park, CO; 10/10/96
- Madison Marshall Award Lecture ; U. of Huntsville, Alabama (11/-15/96)
- American Chemical Society Workshop on Biomedical Polymers, Santa Barbara (11/22-24/96)
- Frontiers of Materials Research Symposium, University of Chicago; Chicago, IL (4/26/97)
- University of Georgia, Athens, GA (5/30-31/97)

## PART II

### Allara

a. Principal Investigator

D.L Allara

b. Current telephone number

c. Cognizant ONR Program Officer: Drs. John Pazik and Larry Cooper

d. Program Objective:

This project involves the work of several co-PIs. This is a program directed toward the development of molecular sized electronic devices and interconnects.

e. Significant results during last year (100-200 words) - **be specific and comment on impact**

\*Developed strategic methods for inserting isolated molecular wire candidates into alkanethiolate self-assembled monolayers on gold and showed (in collaboration with Paul Weiss at Penn State) using scanning tunneling microscopy that the molecular wires had higher conductivities than the background monolayer.

\*Showed that Se-based oligomers attach to gold electrode surfaces to form monolayers ordered even better than with S.

\*Developed high quality, protective monolayer films for GaAs and InP using new methods which work near room temperature in dilute solution. This work now allows attachment of molecular wire candidates to III-Vs and looks promising as a method for electrical and chemical passivation of III-V devices.

f. Brief (100-200 words) summary of plans for next years work

\*Continue molecular wire insertion strategy development for application to micropore devices and will make quantitative measures of single wire conductivities. Will investigate Se and Te attachment. Will develop strategies for selective attachment of multifunctional wires to multi-terminal configurations.

\*Continue III-V passivation work. Will extend attachment to Se and Te to look for improvements.

g. List of names of graduate students and post-doctoral(s) currently working on the project

Carole Mars

Tim Dunbar

Matt Garrett

## Maracas

**Principal Investigator:** Dr. George Maracas  
(602)413-6384

**ONR Program Director:** Dr. John C. Pazik

**Program Objective:** To investigate the application of molecular self assembly to semiconductor manufacture. Our investigations are currently focused on two areas: 1) The use of self assembled monolayers prepared from molecules terminated with perfluorinated *n*-alkyl chains as a means of surface pacification toward air-born particulate contamination. 2) The use of micro-contact printing to prepare functional devices containing sub-micron features.

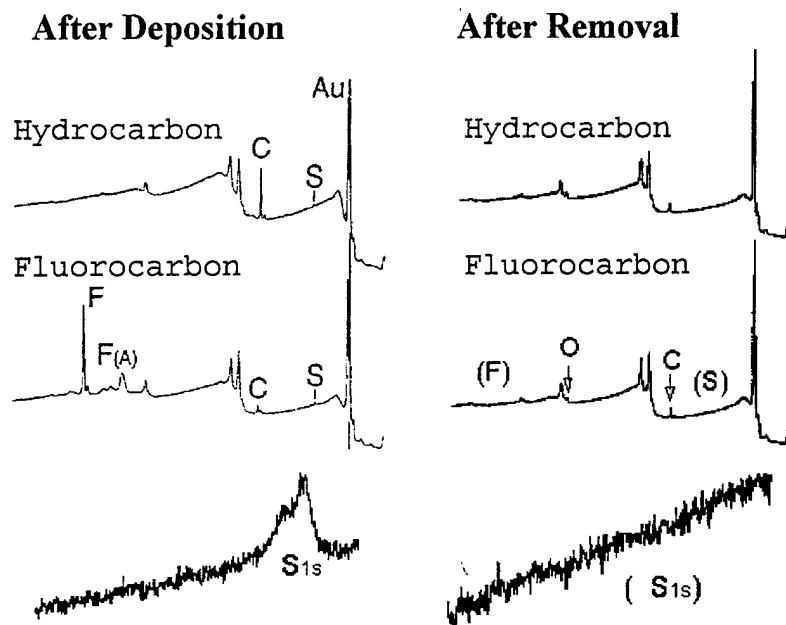
**Surface Pacification.** Self-assembled monolayers with low free energy surfaces are being examined as air-born surface contamination retardants. Successful retardant films must be easily made, as well as, readily and completely removable. The fluorocarbon terminated thiol HSCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub> has been prepared. The self-assembly and surface pacification properties for this compound on gold and GaAs are being compared to those of hexadecanethiol.

The first step in establishing analysis capabilities was to characterize the "bare" gold substrates used to perform the self assembly experiments. The optical constants (spectral ellipsometry) for freshly prepared 1000 Å Au / 50 Å Cr / Si substrates showed excellent reproducibility both within a given lot of wafers and from lot to lot. However, Auger electron spectroscopy indicated that the "bare" gold substrates contained a layer of adventitious carbon contamination ~4 Å thick on the surface.

Taking the carbon contamination layer present on bare gold substrates into account, monolayers prepared from hexadecanethiol had an ellipsometric thickness of  $20.2 \pm 1.3$  Å (literature value: 21.0 Å, uncorrected thickness:  $17.1 \pm 1.3$  Å), indicating complete monolayer formation. Auger spectroscopy and XPS confirmed the presence of C, and S. Monolayers prepared from the fluorinated compound had an ellipsometric thickness of 11.4 Å. The expected length of a fully extended chain was determined by molecular mechanics calculations to be 12.4 Å. Examination of these monolayers by XPS confirmed the presence C, S, and F. Monolayers of comparable quality were formed from ethanol, hexane, and hexadecane. The surface pacification properties of these monolayers is under investigation.



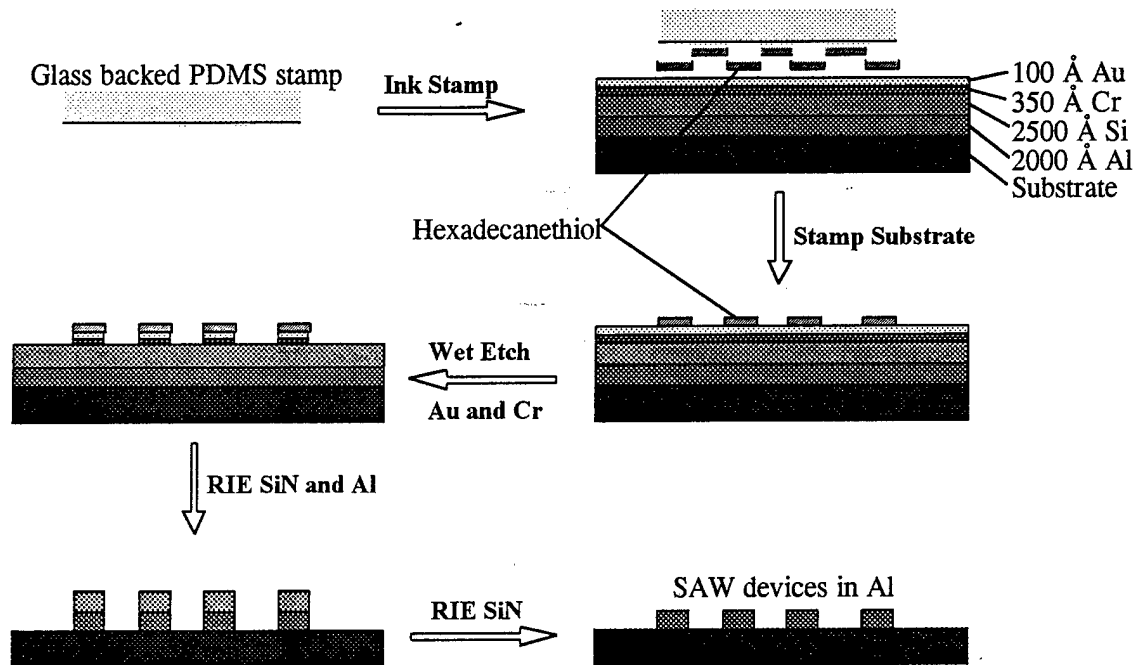
## XPS (ESCA) spectra



Removal of both the hydrocarbon and fluorocarbon monolayers was attempted by UV ozonolysis and oxygen plasma cleaning. In both cases the monolayer was completely removed by oxygen plasma cleaning but not by UV ozonolysis based on XPS analysis for S and F.

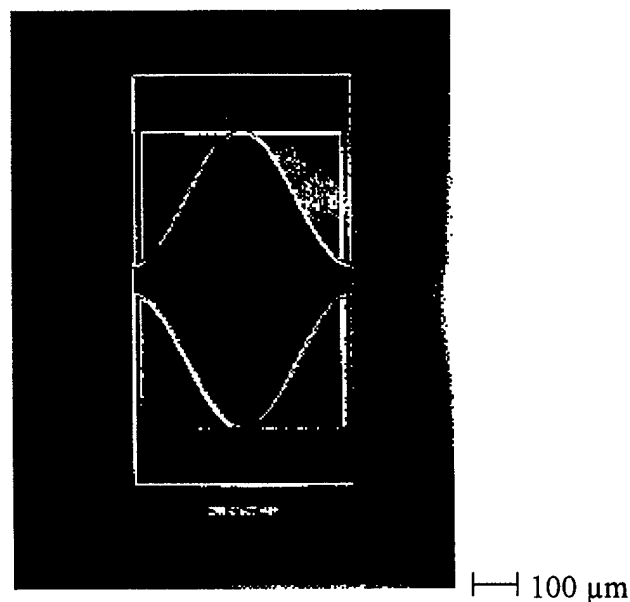
Future investigations will involve examination of the surface passivation properties of fluorocarbon SAMs prepared on gold, GaAs, and SiO<sub>2</sub>. The applicability of this technology to semiconductor manufacturing will also be investigated.

**Micro-contact Printing.** Production of surface acoustic wave (SAW) devices containing sub-micron features by micro-contact printing is also currently being examined. The metal of choice in these devices is aluminum, while micro-contact printing is currently best suited for preparing patterns on gold. Therefore, the patterns are stamped onto gold and then transferred to the underlying aluminum through a series of wet and dry chemical etches (Figure 1). Reactive ion etch of the silicon nitride and aluminum has proved problematic due to incomplete removal of the chromium during the wet etch. Means of overcoming this problem are currently under investigation.



**Figure 1.** Preparation of SAW devices using m-contact printing.

Work to date has primarily involved improvement of the micro-contact printing process itself. A brief outline of the challenges faced in transferring a pattern from the raised features of a polydimethylsiloxane (PDMS) stamp onto a gold substrate are outlined in Table 1. The causes of these problems have been identified, and are being addressed by: 1) The use of a thin PDMS film ( $\sim 10 \mu\text{m}$ ) on a rigid glass support as the stamp (Figure 2). 2) Careful cleaning of the PDMS before use. 3) Use of a patented stamp aligner (prepared in house) to control the pressure exerted by the stamp on the substrate and allow stamping at reduced pressures. The stamp aligner will also allow the registration of the stamped pattern with a pre-existing pattern on the substrate.



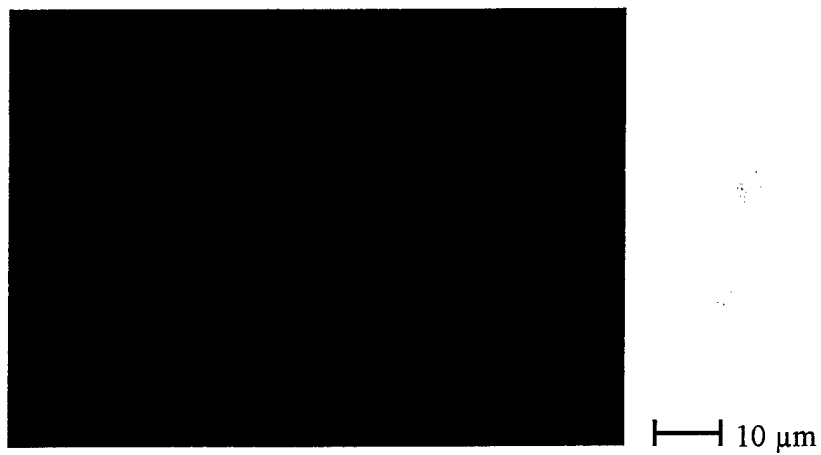
**Figure 2.** SAW device patterned in a thin film of PDMS.

**Table 1. Issues Under Investigation in Micro-contact Printing.**

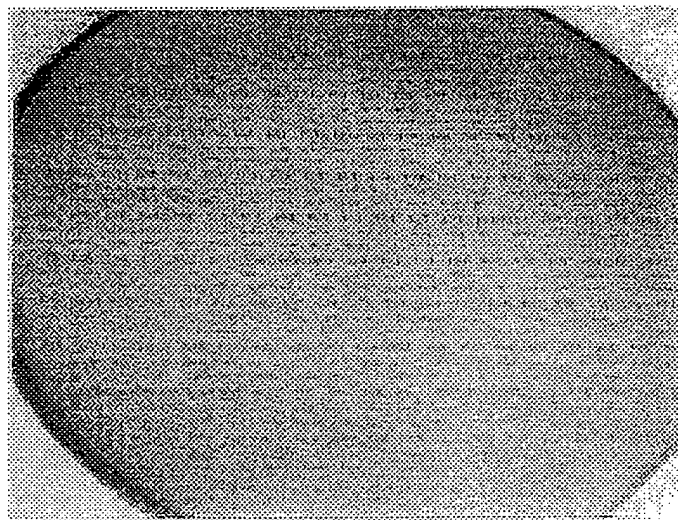
Issues	Solution/Approach	Status
Sagging	Thin glass backed stamp	Essentially eliminated sagging for up to 1 mm sized features
Defects	New stamp cleaning technique	Drastically reduced particulate based defects
Run-out	Thin glass backed stamp	Reduced run-out from 40 $\mu\text{m}/\text{cm}$ to $<0.13 \mu\text{m}/\text{cm}$
Pattern distortion	Pressure control	No visible distortions (line wiggles, line spreading)
Air pockets	Vacuum stamping	Essentially eliminated air pockets
Reproducibility	Pressure control	Provides path to measure/control reproducibility
Registration	x, y, z, q stage	1st generation prototype has been prepared

By carefully controlling the printing parameters tabulated above, high quality patterns such as that shown in Figure 3 can be prepared. These patterns can be produced with good consistency both within a given wafer and from one wafer to the next. Three inch substrates have been successfully patterned using this methodology (Figure 4).

Future work will involve accessing the reproducibility of micro-contact printing using the stamp aligner. A functioning SAW device will be prepared and tested. Application of micro-contact printing toward the preparation of other devices and its value as a semi-conductor manufacture methodology will be examined.



**Figure 3.** SAW device patterned in 200 Å Au / 50 Å Cr on silicon substrates.



**Figure 4.** SAW devices patterned in 200 Å Au / 50 Å Cr on a 3 inch Si wafer.

**Reed**

a. Principal Investigator: Mark A. Reed

b. Phone: (203) 432-4306

c. Cognizant ONR Program Officers: Drs. John Pazik and Larry Cooper

d. Program Objective:

This is a program directed toward the development of molecular sized electronic devices and interconnects.

e. Significant Results during the last year:

1. Measured the electrical properties of a single molecule
2. Developed a novel technique for measuring molecule properties.
3. Measured for the first time the properties of a molecule-metal interface.
4. First preliminary measurement of a molecular RTD

f. Brief summary of plans for next year:

1. Extend the conductance studies through single molecules to the 50 Å regime.
2. Test the wires with tunnel barriers and quantum wells.
3. Determine the efficacy of alligator clips which more closely match the metal probes' Fermi levels and study the surface chemistry of attachment.
4. Build a "molecular heterojunction" database.

g. Those working on this DARPA/ONR project

Mandar Deshpande, Chong-Wu Zhou, Jia Chen, Gabel Chong

## Tour

- a. Principal Investigator: James M. Tour
- b. Phone: (803) 777-9517
- c. Cognizant ONR Program Officers: Drs. John Pazik and Larry Cooper
- d. Program Objective:

This project involves the work of several co-PIs. However, the work of J. Tour has dealt mainly with the preparation of conjugated organic oligomers of precise length and constitution for utilization as interconnects and devices in patterned assemblies and proximal probes. The conjugated compounds must have molecular sized alligator clips for adhesion to the probes. This is a program directed toward the development of molecular sized electronic devices and interconnects.

- e. Significant Results during the last year:

- 5. We demonstrated conductance through a single conjugated oligomer that was isolated from all other conjugated molecules. This was done on a molecule that had been synthesized to a 40 Å length with a single thiol-based molecular alligator clip. The two probes were a gold surface and an STM tip. In order to accomplish this task, we had to develop methods for the sequential deposition of alkane thiol self-assembled monolayers followed by the deposition of the "molecular wires" into the grain boundaries.
- 6. We developed methods for the synthesis of greater than 100 Å molecules on a polymer support, thus streamlining the synthetic protocol.
- 7. We synthesized molecules that may respond as wires with tunnel barriers, wires with quantum wells, and single molecules that may each function as a logic device. In each case, these possess molecular sized alligator clips for attachment to probes.
- 8. We developed a route to organic selenols and organic tellurols (i.e., using selenium and tellurium, respectively, rather than sulfur for thiols) to better approach the Fermi level of metal contacts.
- 9. Prepared and characterized SAMs of organic selenols.
- 10. We developed *ab initio* computational method for assessing metallic probe surface/organic interconnect properties.
- 11. We developed strategies to build molecular CPUs wherein electrostatic potentials may be used as the information carrying packets rather than electrons, thereby significantly reducing the heat requirements.
- 12. We prepared greater than 20 new compounds for testing in Professor Reed's nanopore assembly.

- f. Brief summary of plans for next year:

5. We plan to further extend the conductance studies through single molecules to the 50 Å regime.
6. There are plans to further streamline the syntheses of wires on polymer supports.
7. We hope to test the wires with tunnel barriers and quantum wells.
8. We will construct three-terminal systems.
9. We plan to test the efficacy of alligator clips which more closely match the metal probes' Fermi levels and study the surface chemistry of attachment.
10. We plan to build more molecules with device-like properties and assess their potential properties using *ab initio* methods.

g. Those working on this DARPA/ONR project this summer:

Graduate Students: L. Asplund, S. Huang, D. B. Shortell, Y. Yao, A. Rawlett  
Postdocs: J. Seminario, W. Reinerth

## EOY Report - PART II

- a. Principal Investigator: George M. Whitesides
- b. Current Telephone Number: 617-495-9430
- c. Cognizant ONR Program Officer: Dr. John Pazik
- d. Program Objective:
  - To develop new processes for making micro-and nanostructures using:  
soft lithography  
conformal, contact, phase-shift lithography
  - To make electronic test structures using these techniques

e. Significant Results During the Last Year:

The major accomplishments in the last year have been to begin to demonstrate the capabilities of soft lithography as a technique for forming functional microelectronic systems. We have demonstrated the fabrication of arrays of HEMTs in GaAs/AlGaAs, of MOSFETs in Si/SiO<sub>2</sub>, and of Schottky diodes. The feature sizes in these structures are large--20  $\mu\text{m}$ --but this dimension is set by the size of the patterns we were using, and is not an intrinsic limitation of the soft lithographic technology. The two transistors required 3 layers of fabrication, and registration to within <10  $\mu\text{m}$ . These structures demonstrate clearly that soft lithography is compatible with the processes used in microelectronic fabrication. In another part of this research, we have examined a key unresolved issue in soft lithography: that is, the ability to achieve registration over significant areas. Using an optical technique based on Moiré patterns, we have demonstrated that two layers of patterning can be registered to < 0.5  $\mu\text{m}$  (the limits of resolution of this technique) over areas of several mm<sup>2</sup>. Further studies of registration will require suitably designed registration patterns. A third theme in the research has been photolithographic. We have developed techniques for using the transparent stamps developed for soft lithography as phase shift masks for conformal, contract phase shift lithography: using this technique, we have produced features with dimensions less than 50 nm.

### IMPACT:

This work provides an alternative to photolithography for microfabricators. It will result in cost effective methods for producing microstructures of interest in DoD applications (electronic systems in non-planar geometries for UAV and UUVs; plastic display systems for new soldier systems; laboratory on a chip technology for BW/CW defense.

- Alternatives to photolithography for fabrication of large-area, non-planar, 3-D, integrated electronic/MEMS/Optical systems
- Practical new route to certain types of nanostructures



f. Brief Summary of Plans for Next Year:

We propose to continue the exploration and development of soft lithography, focusing on work in three areas.

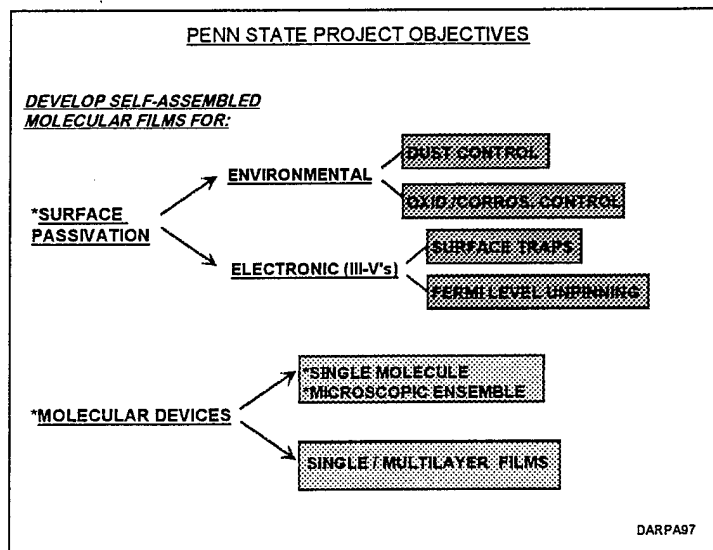
- Establishing the minimum obtainable feature size in soft lithography  
In current work using  $\mu$ CP, in an unprotected laboratory, we are reliably able to achieve 400-nm feature sizes, and less reliably, 100-nm feature sizes; there is no indication that these are minimum dimensions.. We intend to explore several of our systems to determine the minimum feature size that can be obtained, and to examine the interplay between the physical properties of the elastomer used in the stamp and the patterns it can produce.
- Prototyping Devices  
We have prototyped a number of new types of lithography based on the fundamental concept of an elastomeric stamp and contact printing. We propose to explore and develop these concepts as an advanced exploratory program. We will prepare computer components (e.g. , transistors and arrays) and simple functional systems (e.g., ring oscillators) to develop engineering demonstrations.
- Pattern Transfer to Non-Planar Surfaces.  
We intend to develop microcontact printing as a method to pattern features at the 200 nm - 2  $\mu$ m feature size on highly curved exterior surfaces (especially the exterior surfaces of optical fibers), on interior surfaces, and on important classes of curved surfaces (e.g. optical lenses).

g. Names of Graduate Students and Postdoctoral Fellows currently working on the project.

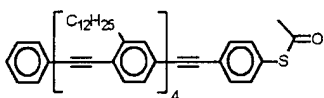
Xiao-mei Zhao  
Tao Deng  
Joe Tien

## Part III

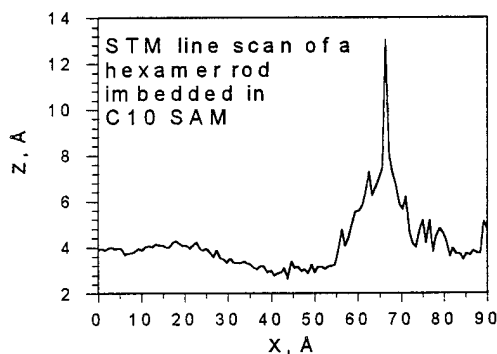
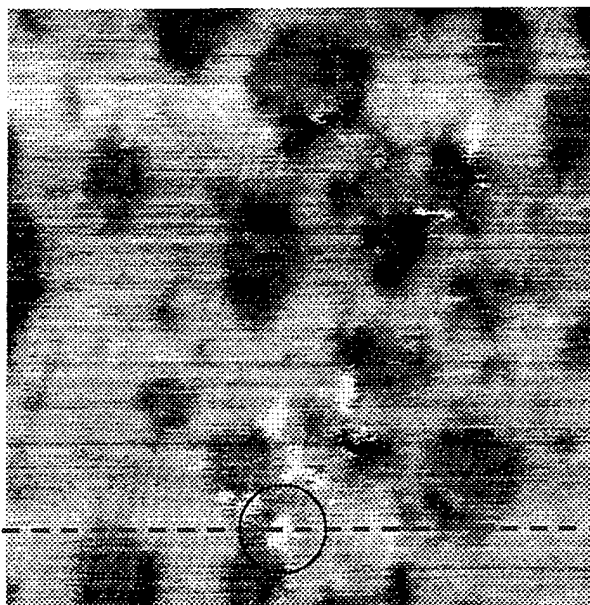
Allara



Hexamer Oligomer  
( $\sim 0.005 \mu\text{m}$ )



(Synthesis:  
J. Tour, USC)



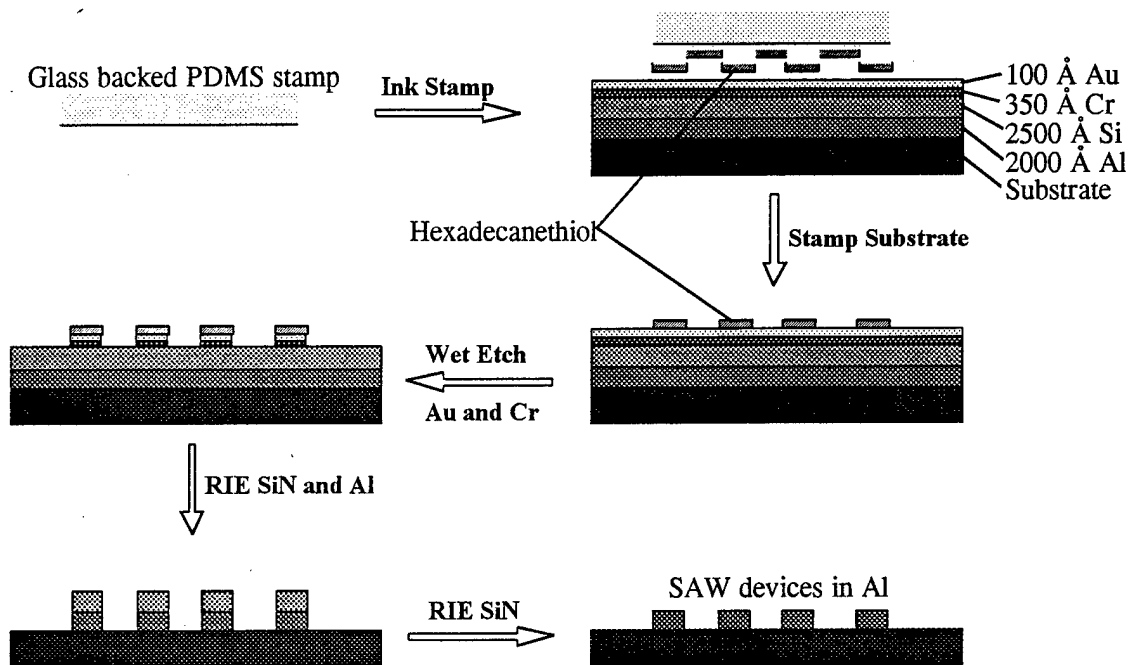
**Accomplishment:** \*Devised method for attaching isolated oligomers in inert SAM (D.Allara, PSU)

\*Measured enhanced conductivity of oligomer by STM (P. Weiss, PSU)

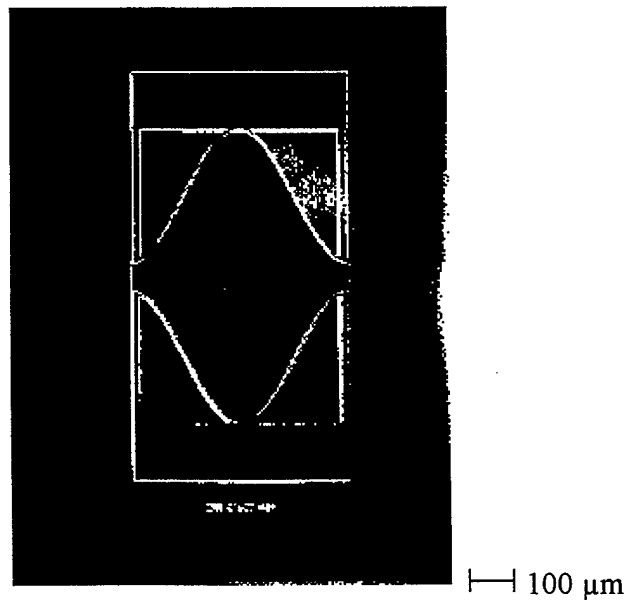
**Impact:** \*Established basis for self-assembly attachment of molecular wire candidates at Au nanoprobles.

\*Established oligomer device feasibility

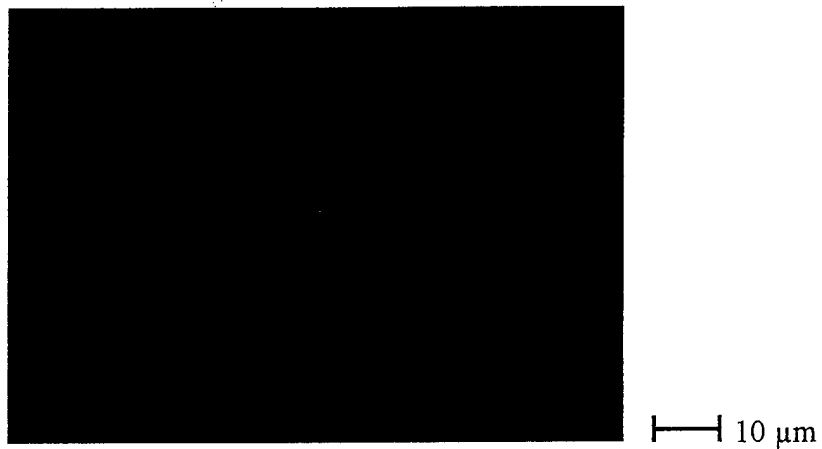
## SAW devices using $\mu$ -contact printing



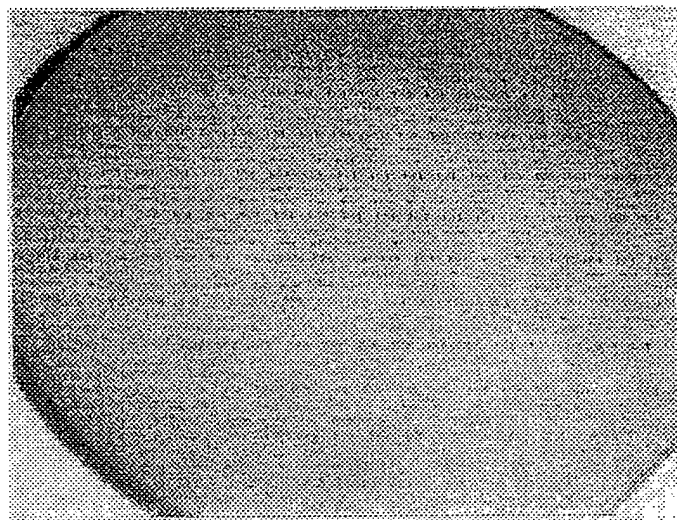
## SAW device patterned in a thin film of PDMS



**SAW device patterned in 200 Å Au / 50 Å Cr on silicon substrates.**



**SAW devices patterned in 200 Å Au / 50 Å Cr on a 3 inch Si wafer.**



## Self-Assembly Based Approaches to Microelectronic Fabrication & Devices

### Objective

To develop self-assembling structures and processes for use in microelectronics fabrication and systems.

### Approach

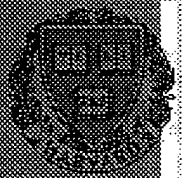
•soft lithography and micro-contact printing  
electrically functional self-assembling devices

### Accomplishments

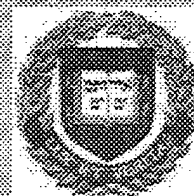
- Fabrication of functional devices (FETs, SAW) using microcontact printing
- Developed synthesis of molecular transistors
- Demonstration of single molecule conductor and molecular RTD

### Schedule

- Demonstrate production-quality SAW devices & yield
- Engineer molecular contacts for device improvement
- Create self-assembly contact "database"

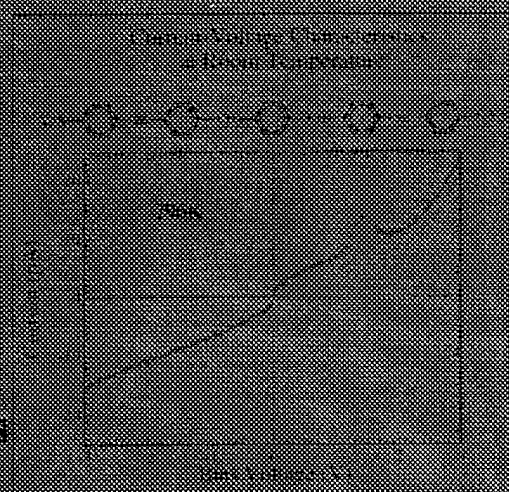


**Yale University (M. Reed, PI)**



## **Electrical properties of molecular devices**

- **Objective:** develop synthesis and techniques for self-assembled molecular devices
- **Accomplishments:**  
Measurement of molecular electronic transport properties, first molecular device (RTD)
- **DOD Relevance**  
Creation of molecular electronic devices for ultradense systems
- **Possible Payoff**  
Self-assembling molecular devices and interconnects



## Tour

### **Self-Assembly Based Approaches to Microelectronic Fabrication and Devices: Surface Passivation, Soft Lithography, Electrically Functional Systems, and Hierarchical Self-Assembly**

**OBJECTIVE:** To prepare interconnects and devices in the nanoscale regime from single organic molecules.

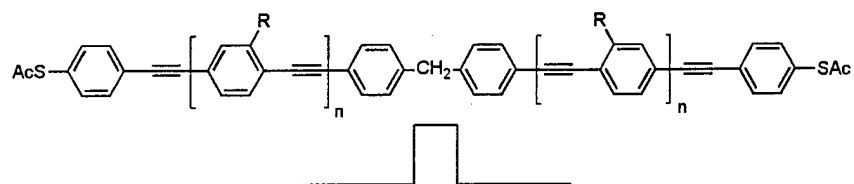
**APPROACH:** The use of synthetic organic chemistry to construct these new nanoscale architectures.

#### **ACCOMPLISHMENTS:**

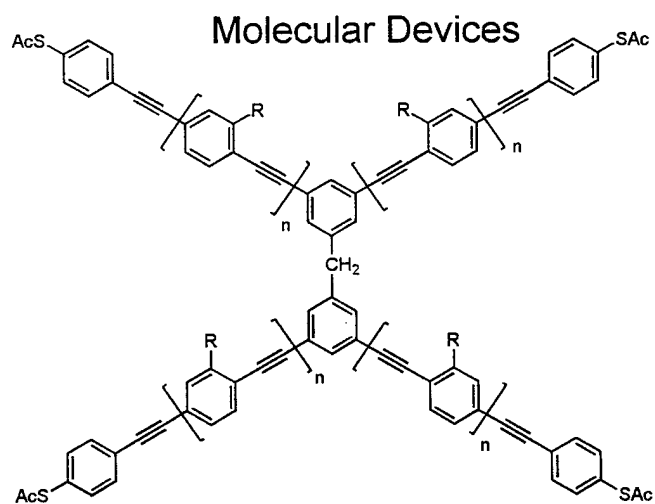
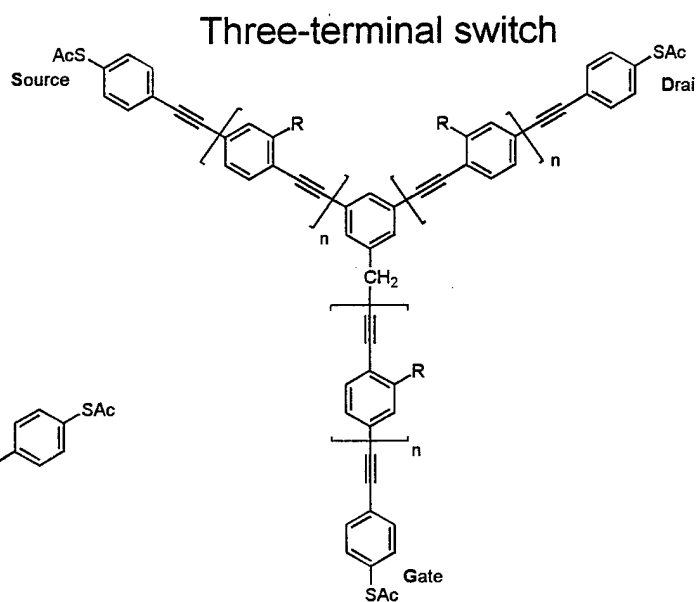
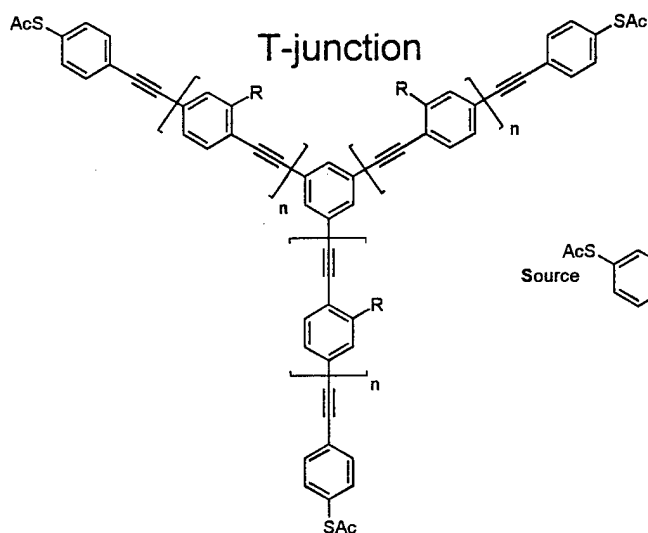
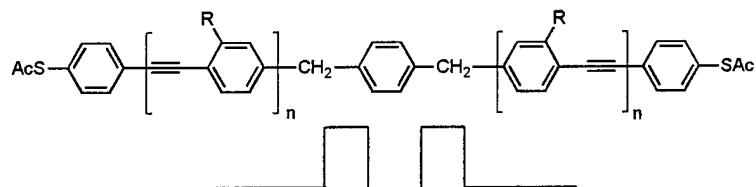
- Demonstration of conductance through a single conjugated oligomer that was isolated from all other conjugated molecules. This was done on a molecule that had been synthesized to a 40 Å length with a single thiol-based molecular alligator clip. The two probes were a gold surface and an STM tip.
- Synthesized molecules that may respond as wires with tunnel barriers, wires with quantum wells, and three and four terminal logic and switch-like molecules. In each case, these possess molecular-sized alligator clips for attachment to probes (see viewgraph).
- Developed a route to organic selenols and organic tellurols (i.e., using selenium and tellurium, respectively, rather than sulfur for thiols) to better approach the Fermi level of metal contacts. SAM formation from these systems was studied.
- We developed *ab initio* computational method for assessing metallic probe surface/organic interconnect properties.
- Developed strategies to build molecular CPUs wherein electrostatic potentials may be used as the information carrying packets rather than electrons, thereby significantly reducing the heat requirements (see viewgraph).
- Prepared greater than 20 new compounds for testing in Professor Reed's nanopore assembly.



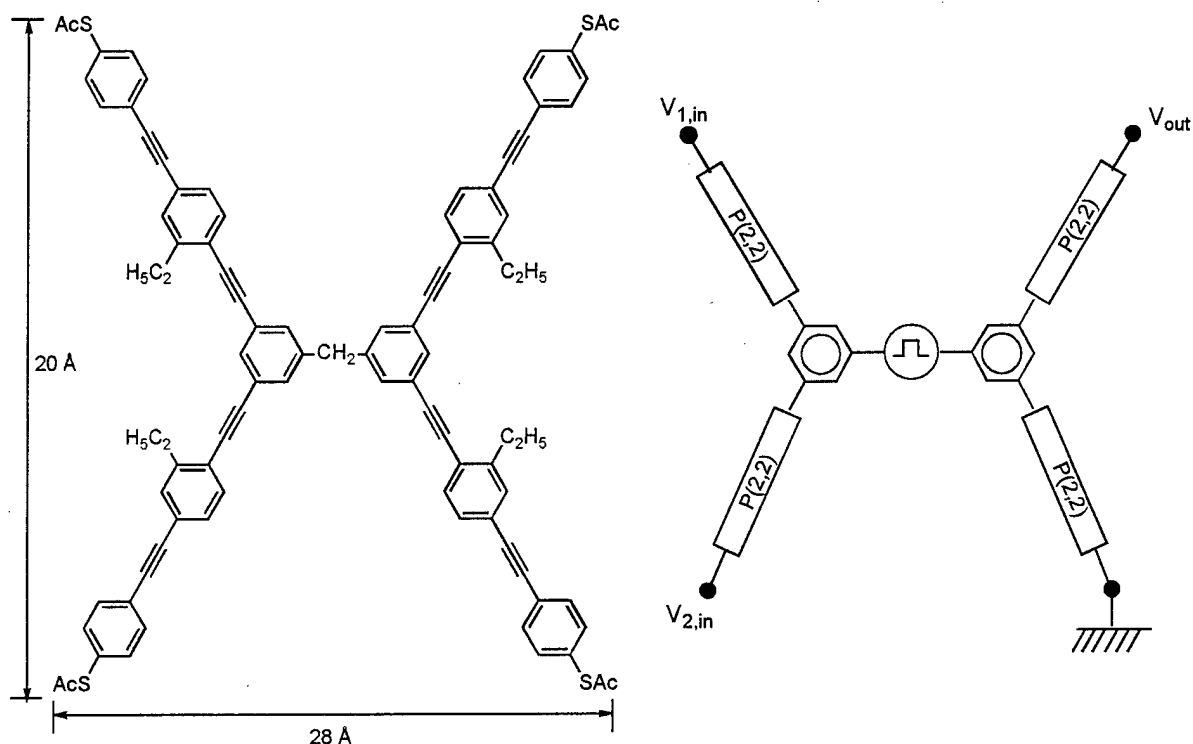
### Molecular wire with tunnel barrier



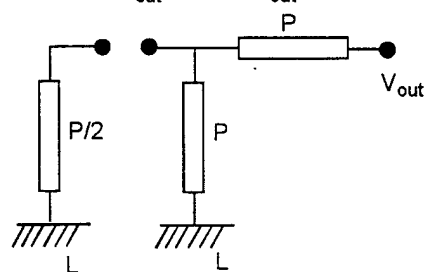
### Molecular wire with quantum well



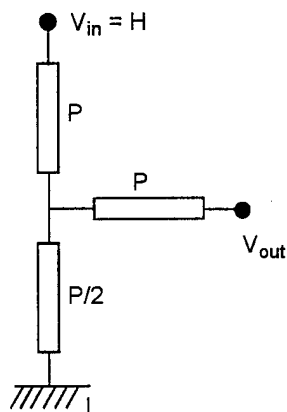
# Chemical structure and its corresponding molecular device configuration and truth tables



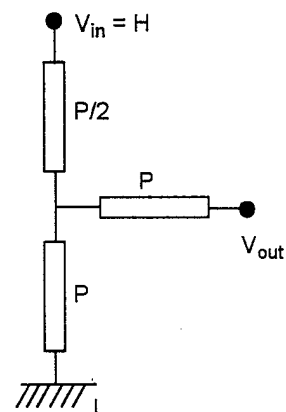
If  $V_{1,in} = L$  and  $V_{2,in} = L$   
then  $V_{out} = L$  and  $Z_{out} \sim 2P$



If  $V_{1,in} = L$  and  $V_{2,in} = H$   
then  $V_{out} = L$  and  $Z_{out} \sim (4/3)P$



If  $V_{1,in} = H$  and  $V_{2,in} = H$   
then  $V_{out} = H$  and  $Z_{out} \sim (4/3)P$



If the output is active (as a potential)

$V_{1,in}$	$V_{2,in}$	$V_{out}$
L	L	L
L	H	L
H	L	L
H	H	H

AND (OR if negative logic is used)

If the output is passive (as an impedance)

$V_{1,in}$	$V_{2,in}$	$Z_{out}$
L	L	H
L	H	L
H	L	L
H	H	L

NOR (NAND if negative logic is used)

Explanatory text for PART III:

**(Scheme 1)** Synthesized molecules that may respond as wires with tunnel barriers, wires with quantum wells, and three and four terminal logic and switch-like molecules. In each case, these possess molecular-sized alligator clips for attachment to probes.

**(Scheme 2)** Developed strategies to build molecular CPUs wherein electrostatic potentials may be used as the information carrying packets rather than electrons, thereby significantly reducing the heat requirements. The molecule shown may act as a logic device as described with the corresponding circuit diagrams.

## EOY Report - PART III

- a. Introductory 5-Part Viewgraph
- b. Two supporting Viewgraphs
- c. Explanatory Text

### Viewgraph 1:

The major accomplishments in the last year have been to begin to demonstrate the capabilities of soft lithography as a technique for forming functional microelectronic systems. We have demonstrated the fabrication of arrays of HEMTs in GaAs/AlGaAs, of MOSFETs in Si/SiO<sub>2</sub>, and of Schottky diodes. The feature sizes in these structures are large--20  $\mu\text{m}$ --but this dimension is set by the size of the patterns we were using, and is not an intrinsic limitation of the soft lithographic technology. The two types of transistors required 3 layers of fabrication, and registration to within <10  $\mu\text{m}$ . These structures demonstrate clearly that soft lithography is compatible with the processes used in microelectronic fabrication. In another part of this research, we have examined a key unresolved issue in soft lithography: that is, the ability to achieve registration over significant areas. Using an optical technique based on Moiré patterns, we have demonstrated that two layers of patterning can be registered to < 0.5  $\mu\text{m}$  (the limits of resolution of this technique) over areas of several mm<sup>2</sup>. Further studies of registration will require suitably designed registration patterns. A third theme in the research has been photolithographic. We have developed techniques for using the transparent stamps developed for soft lithography as phase shift masks for conformal, contract phase shift lithography: using this technique, we have produced features with dimensions less than 50 nm.

### Viewgraph 2:

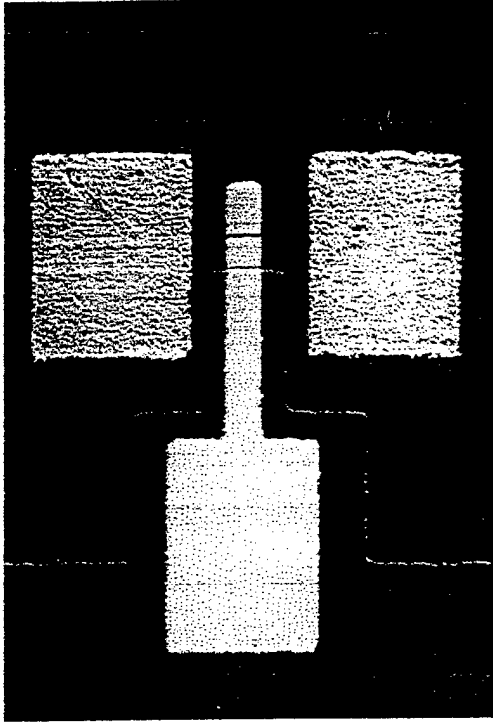
Figure (a) shows an array of p-channel Metal Oxide Semiconductor Field Effect Transistors (MOSFETs) with 20  $\mu\text{m}$  gate length and 400  $\mu\text{m}$  gate width fabricated using MIMIC. Three registered MIMIC steps were involved. First two steps involved using MIMIC of polyurethane to open regions in SiO<sub>2</sub> for source and drain formation and for making contacts thru the gate and field oxides. The last step used MIMIC in patterning Al metallization by lift-off. The drain-source characteristics of a representative p-MOSFET is shown in Fig.(b). The threshold voltage was -2V. These characteristics were similar to those fabricated using photolithography. Our results show that soft lithography is compatible with standard silicon device fabrication techniques. Furthermore, soft lithography can be applied in fabricating devices on non-planar or flexible substrates.

### Viewgraph 3:

Elastomeric phase masks were prepared by casting and curing poly(dimethylsiloxane) against silicon (100) wafers whose surface had been patterned with a photoresist film of an appropriate relief structure by conventional photolithography. The thickness of the photoresist films and the corresponding depth of the surface relief of the phase masks was  $0.4\text{--}0.5\text{ }\mu\text{m}$  ( $\sim\pi$  phase shift for wavelengths emitted by a mercury lamp). The geometry of the mask relief can be varied extensively, using mechanical compression and replica molding. By exposure of photoresist to light passing through an elastomeric phase mask in conformal contact with the resist, patterns with feature sizes as small as 50 nm can be rapidly formed over large areas using broadband ( $\lambda = 330\text{--}460\text{ nm}$ ) incoherent light. Figure shows scanning electron micrographs of lines in photoresist formed by near-field contact-mode photolithography using elastomeric phase masks with grating test patterns of different periods  $p$  and linewidths  $w$ . We believe that near-field contact-mode photolithography using elastomeric phase masks provides a remarkably convenient method that extends the application of UV photolithography to the deep sub-100 nm range.

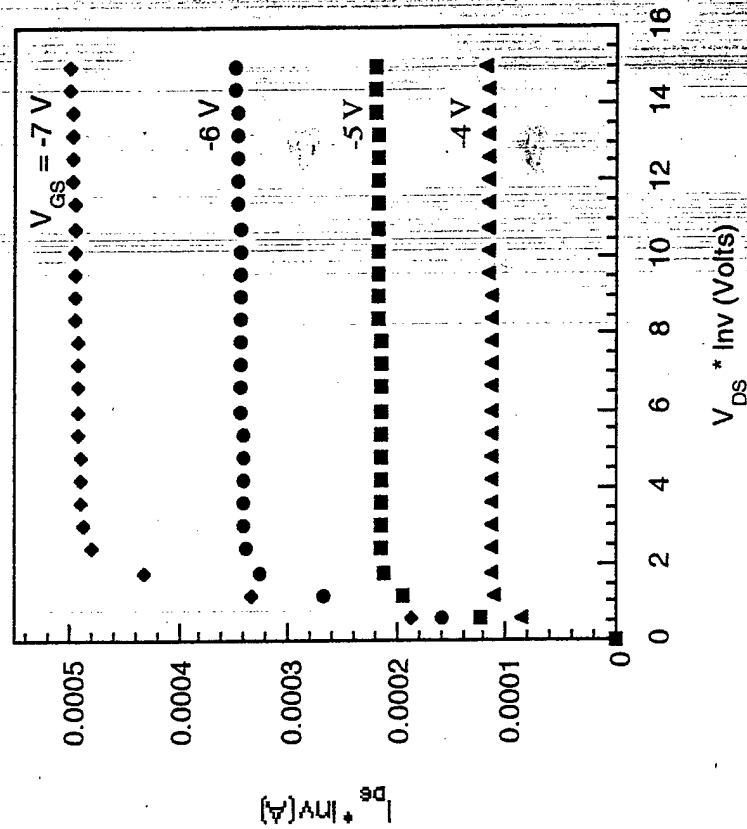
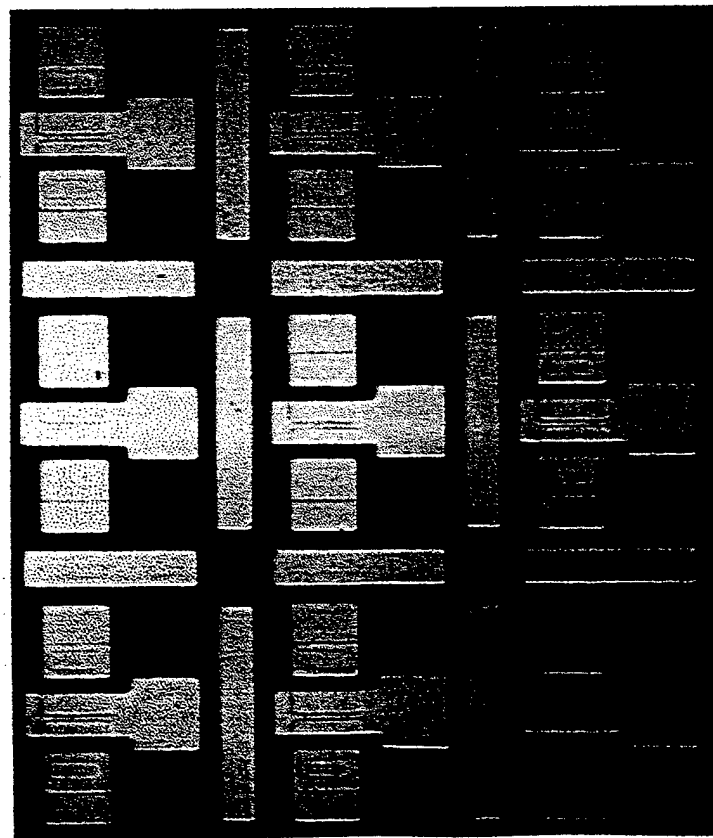
## Viewgraph 1

George M. Whitesides, PI

<p><b><u>Role in Project</u></b></p> <ul style="list-style-type: none"><li>• Development of new methods and materials of fabrication</li></ul> <p><b><u>Technical Approach</u></b></p> <ul style="list-style-type: none"><li>• Soft Lithography: Contact printing, Replica and Micromolding, Capillary Molding, Conformal Phase Shift Lithography</li></ul>	<p><b><u>Accomplishments</u></b></p> <ul style="list-style-type: none"><li>• Fabrication of HEMTs (GaAs/AlGaAs) and MOSFETs (Si/SiO<sub>2</sub>) by Soft Lithography: 20<math>\mu</math>m Feature Size</li><li>• 3-Level Fabrication</li></ul> 
<p><b><u>Impact</u></b></p> <ul style="list-style-type: none"><li>• Engineering demonstrations to decrease barrier to development and adoption of soft lithography</li></ul>	

# Viewgraph 2

George M. Whitesides, PI



# Viewgraph 3

George M. Whitesides, PI

